HIGH POWER BIPOLAR LEAD-ACID BATTERIES

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INTRODUCTION

The Jet Propulsion Laboratory (JPL), with interest in advanced energy storage systems, has been involved with the development of a unique lead acid battery design. This battery utilizes the same combination of lead and lead dioxide active materials present in the automobile starting battery. However, it can provide 2-10 times the power while minimizing volume and weight. The typical starting battery is described as a monopolar type using one current collector for each plate. The bipolar battery uses a single current collector for both the positive and negative plate of adjacent cells. Specific power as high as 2.5 kW/kg has been projected for 30 second periods with as many as 2000 recharge cycles.

BACKGROUND

In a 1985 study prepared for the Department of Energy (1), 34 alternative five-passenger advanced vehicles were ranked using multi-attribute decision analysis. The ranking, designed to ascertain the most promising battery EV technology/range combinations, indicated that the bipolar lead-acid 100-mile-basis of the ranking was the exceptionally high power capability, excellent thermal characteristics, well known chemistry, low cost, large industrial base and potential to develop the technology. A number of patents have been issued on various aspects of the cell and battery technology.

In July of 1986, a program was initiated at JPL under the sponsorship of the Air Force Wright Aeronautical Laboratories for the development of a high specific power, 50-kW, sealed bipolar lead-acid batter. This four-year program was the result of the A.F. interest in the JPL bipolar lead-acid technology developed during the mid 1980s. In the fall of 1990, three 50 kW modules of a quasi-bipolar design (a modification of the true bipolar battery), based on the JPL technology, were assembled under a subcontract to Johnson Controls Incorporated. At this writing, one was delivered to the A.F. for testing.

DESCRIPTION OF SYSTEM

The unique aspects of this technology are the sealed bipolar construction and the light weight composite biplates utilizing electrically conductive tin dioxide coated glass fibers.

The basic building block (Figure 1) of the bipolar design is a light-weight composite bipolar plate (biplate) consisting of two layers (substrates). One layer is composed of conductive tin oxide-coated glass fibers and the other of carbon fibers, each embedded in its own polymeric matrix. The negative substrate consists of a conductive carbon fiber or powder filled impervious thermoplastic composite. It serves as the current collector (substrate) for the negative plate (Pb). The carbon-based materials are commercially available. The unique positive substrate serving as the current collector for the positive electrode (PbO₂) consists of tin dioxide coated glass fibers (Figure 2) or powders imbedded in a non-porous thermoplastic and molded into a composite to provide the necessary conductivity. At the present time, commercial sources of tin dioxide coated fibers are not available. The substrates must be capable of allowing electrons resulting from the discharge reactions to transfer from the negative active materials of one cell to the positive active materials in the adjacent cell (and in reverse during charge).

A cell (Figure 3) consists of the positive side of one biplate facing the negative side of the adjacent biplate. Between the active materials in each cell is a porous glass mat separator which serves as a reservoir for the electrolyte and to physically separate the positive and negative active materials. The biplates assembled in series are sealed at their periphery and together with the current collector endplates produce the sealed battery. The design is such that the current travels from one end of the battery directly through the biplates to the negative end. There are no tabs or cell terminals which minimizes the resistance to current flow.

DESIGN CONSIDERATIONS

The requirement of maximum specific power dictates a bipolar construction in order to eliminate resistance through the lead grid of conventional lead-acid batteries. For any application, either terrestrial or space, such a battery also needs to be sealed, as watering would be impractical because of the large number of very thin cells required for a multi-kW battery. Lead has been the commonly used substrate for preparation of the bipolar plates in previous lead-acid batteries, but the weight of lead is unacceptable in minimum practical thicknesses.

Currently, the conductive glass fibers are produced by spraying a solution of tin tetrachloride in the presence of air on a heated glass fiber mat $(500^{\circ}C)$. This process, known as spray pyrolysis, has long been a production method for applying transparent tin dioxide (SnO_2) conductive thin films to glass. In this instance, glass fibers of 10 micron diameter are coated with 0.5 to 1 micron of conductive tin oxide. The material has been shown to be thermodynamically stable with respect to oxidation or reduction at the positive electrode in normal operation. The material will never be life-limiting when used in the positive plate environment if care is taken to prevent reversal of the positive plates. The new light-weight plastic composites developed by JPL have an overall thickness of 0.06 cm. The goals of the volume resistivity of 1 to 2 ohm-cm and an area density of 0.15 g/cm² have been achieved.

The capability for sealing is provided by the gas recombination mechanism associated with the "starved" cell design. That is, unlike the typical automotive starting battery, there is no free flowing electrolyte. All of the sulfuric acid electrolyte is contained in the pores of the active materials and separator allowing for gas to freely circulate in each cell. The sealing can be accomplished because the oxygen gas generated on over charge at the positive electrode is recombined at the negative electrode in the same cell, thus, minimizing gas pressure. The design requires the appropriate balance between the capacities of the positive and negative plate in each cell.

ADVANTAGES

The fundamental advantage of the bipolar lead-acid couple for high power applications is due to four characteristic: high open circuit voltage, low electrolyte resistivity, very low cell-to-cell resistance, and discharge with an increase in entropy. Very few couples can match the power capability of the lead-acid system (given by the ratio of the square of the open circuit voltage to the electrolyte resistivity) and most couples discharge exothermically. Because of the increase in the entropy of the system during discharge, the lead-acid battery will absorb heat during discharge. Furthermore, the sealed bipolar lead-acid battery described above has the advantages of very light weight construction, a thermodynamically stable conductor in the bipolar plate, and the absence of auxiliary equipment such as pumps, cooling loops, and heavy storage containers required by several other battery systems.

FUNDAMENTAL CONCEPTS

The important value of specific power (kW/kg) of a high power battery can be factored into two parts: the surface power density (W/cm^2) and the specific area (cm^2/kg) . Batteries very often perform well in one factor but generally do not fare well in both characteristics. For comparison purposed, the maximum surface power density for an electrochemical cell can be expressed as a figure of merit, M, as given by:

$$M = \frac{(E'oc)^2}{\rho}$$
(1)

where E'oc is the battery voltage extrapolated to zero current from the polarization curve, and ρ is the electrolyte resistivity. For comparison, M is calculated for nine different couples and shown in Table 1. Based on intrinsic properties of the couple alone the lead-acid system has three times the surface power density of the Ag-Zn and four time the Ni-H₂ and Ni-Cd system.

For maximum specific power the area factor must be a maximum. This can only be accomplished by minimizing the thickness and weight of the components. This is done by use of a light weight bipolar plate and the use of thin layers of active material for the electrodes.

Table 1 also shows the calculated value for the quantity Q/E which is the ratio of thermal (Q) to electrical (E) energy when discharging at 2/3 E'oc. The values for Q/E ratio are consistent with those projected from thermodynamic considerations and show a clear superiority of the lead-acid system, i.e., there is a lower heat generation for the electrical energy generated.

PERFORMANCE PROJECTIONS

The mean specific power (MSP) of the battery can be represented by:

$$MSP = \frac{E_d i}{M}$$
(2)

where E_d is the discharge voltage, i is the current density and M is the total battery mass per unit of plate area. The current density is related to the discharge time (t_d) by:

$$i = \frac{0.2241 \text{ m}^{+} \text{ u}^{+}}{t_{d}}$$
 (3)

The factor 0.2241 is the Ah/g of positive active material (limiting electrode), and m + and u + are the mass/area (g/cm²) and utilization efficiency of the positive active material (PAM) respectively.

Computer generated plots of the relationship between MSP and positive plate thickness are given in Figure 4 for various pulse lengths. The projections also include the effect varying the mass/area and resistance of the positive active material. These curves show that the required pulse length will dictate the thickness of the positive active material and that the mass reduction has a greater effect than the resistance.

STATUS OF HARDWARE DEVELOPMENT EFFORT

The designs for the bipolar plate and the battery were under development at JPL from 1986 to 1988, culminating with the construction of a small 6-cell bipolar battery and the fabrication of several versions of a light-weight composite bipolar substrate. In August, 1988, the responsibility for the A.F. effort of scaling up the design of the battery was assigned to Johnson Controls, Inc. (JCI), in Milwaukee. Under JPL's management, all critical areas in the development of the battery were addressed by JCI in three parallel tasks.

At the component level, the key critical area of development of a light weight bipolar substrate and frame stable in the environment of the lead-acid battery received the most emphasis. JCI developed a 2-layer substrate consisting of a thin carbon filled polyethylene layer for the negative side, bonded to a thin conductive tin oxide coated glass fibers filled plastic layer for the positive side. The use of thin coatings of lead to enhance the adhesion of the active materials to the conductive plastics was also investigated.

At the cell level, several critical aspects such as active materials formulation, separator selection, thin electrodes pasting and formation, sealed construction and gas recombination, were tested for refinements and improvements. At the battery level, critical factors such as module sizing and voltage, thermal management, battery configuration, termination, current collection and light weight end block support, were investigated experimentally and were also explored using JCI's comprehensive computer model for the leadacid battery. The battery design specifications are given in Table 2. The drawings and a photograph are given in Figures 5 and 6.

A modified 50-kW bipolar battery was delivered to the Air Force in September 1990 and is currently under test. Some compromises were made to meet the delivery schedule. The delivered design was a package containing 4-20 cell batteries in series. One major deficiency was in the biplate design, i.e., the biplate was a quasi-bipolar (folded screen) design and contained no stannic oxide fibers. Also, the plate area was reduced by half and the thickness of the active material increased for simplified assembly. This provided the required capacity but reduced the power capability.

Despite these significant deficiencies, the initial results showed considerable promise: the battery demonstrated a specific power in excess of 1 kW/kg for short discharges on the order of a few seconds, or more than twice the specific power achieved to date with conventional high power lead-acid batteries.

ELECTRIC VEHICLE CONSIDERATIONS

The electric vehicle battery must satisfy numerous requirements including high specific power and energy, high reliability, low cost and maintainability and long cycle life at high depths of discharge. To these ends, the sealed bipolar lead-acid battery containing the stannic oxide material offers some new alternatives for potential use in the EV arena. Higher values of specific power and specific energy have been demonstrated when comparing with the lead-acid starting, lighting, ignition (SLI) battery. Simplicity of manufacturing this sealed battery offers comparable if not improvements in cost, reliability and maintainability. One other attribute is the endothermic property of the lead-acid system when it is discharged. This characteristic will result in less complexity of battery design compared to other batteries that are exothermic on discharge.

The subject of long cycle life at high depths of discharge must be addressed. This critical area is a function of several cell design factors, most notably the active material formulation. Most manufacturers tend to use their stock or patented materials; however, innovation will be required to design for this specific application. Substantial improvements in performance were obtained in preliminary experiments by the JPL Battery System Group with the addition of small amounts of tim oxide to the positive active mass.

There are two alternatives for using this battery in an EV application. One is the use of this battery as the main power source. Tradeoffs in design are required to balance all the factors. For acceleration the present high power design would be ideal; for distance, high capacity is required. Designing for both is possible with appropriate compromises. The second alternative involves the hybrid concept. The power system would utilize the Sealed Bipolar Lead-Acid Battery for acceleration together with a second power source for extended range. The second power source could be a deep discharge lead-acid battery, a fuel cell battery or even a small internal combustion (IC) engine.

Several studies have concluded that both EV alternatives including those with the range extenders are feasible. While improvements in these systems are required, with a properly designed sealed true-bipolar plate lead-acid battery containing the stannic oxide additive and the correct thickness/area balance and formulation of active materials, one of the major hurdles for an EV battery may have been cleared.

REFERENCES

- 1. "Advanced Vehicle Systems Assessment", JPL Publication 84-79, prepared by the Jet Propulsion Laboratory, California Institute of Technology, for the Department of Energy, (1984).
- U.S. Patents, 4,098,967 (1978); 4,275,130 (1981); 4,353,969 (1982); 4,405,697 (1983); 4,507,372 (1985); 4,510, 219 (1985); 4,539,268 (1985); 4,542,082 (1985); 4,547,443 (1985); 4,625,395 (1986); and 4,658,499 (1987).

L

- CONDUCTIVE (< 2 OHM-CM)
- LIGHTWEIGHT (< 150 MG/CM*)
- THIN (0.025" (0.0635 CM))
- CONDUCIVE TO ELECTRODE ADHESION
- · PORE FREE
- · ELECTROCHEMICALLY STABLE AT POO, POTENTIAL
- · LOW SOLUBILITY IN SULFURIC ACID
- HIGH OXYGEN OVERPOTENTIAL
- . LOW COST



Figure 1. Bipolar Plate Design Goals



Figure 2. SnO2 Coated Glass Fibers





Q/E IS THE RATIO OF THERMAL TO ELECTRICAL POWER AT 2/3 E' oc

(1) VALUE AT 30 C (2) VALUE AT 450 C (3) VALUE AT 450 C (4) VALUE AT 100 C (5) VALUE AT 18 C (6) VALUE AT 50 C

*EXTRAPOLATION FROM E - I CURVES

• OPEN CIRCUIT VOLTAGE USED BECAUSE OF LOW ACTIVATION POLARIZATION • • M = FIGURE OF MERIT = (E' oc) $^{2/\rho}$

Figure 3. Bipolar Electrode Configuration

Table 1. Characteristics of Electrochemical Couples



Figure 4. Specific Power vs. Positive Plate Thickness and Pulse Length

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Figure 5. JPL/JCI/Air Force 50KW Module

Number of cells	80
Dimensions	10.6"x12.8"x11"
Weight	43.1 Kg
Substrate thickness	0.020"
Frame thickness	0.098"
Cell thickness	0.102"
Active area	521 cm2
Grid open area	82%
Grid thickness	0.020"
Acid density	1.305
Acid amount/cell	80 ml

Table 2. Battery Design Specifications



Figure 6. Photograph of the 50 KW Module